

# PATENT SPECIFICATION

(11) 1 550 168

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- (21) Application No. 18634/76 (22) Filed 6 May 1976  
 (31) Convention Application No. 7 501 075  
 (32) Filed 6 May 1975 in  
 (33) France (FR)  
 (44) Complete Specification published 8 Aug. 1979  
 (51) INT CL<sup>2</sup> C25D 3/16//C07C 101/28, 143/16  
 (52) Index at acceptance  
 C2C 200 202 20Y 290 29Y 30Y 323 32Y 360 361 362 364 366 367  
 368 36Y 394 39Y 620 623 624 628 630 80X LU RK  
 C7B 120 436 444 445 446 450 452 456 458 461 644 727 DK

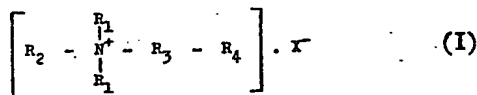


## (54) BRIGHT NICKEL ELECTROPLATING BATH

(71) I, FRANCINE POPESCU, a French national, of 32 rue E. Dolet, 94100-Saint Maur, France, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

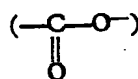
The invention relates to the electrodeposition of bright nickel from aqueous, acidic nickel electroplating baths, and to brighteners and additives to be used in such baths.

The invention provides an aqueous, acidic nickel electroplating bath which comprises a source of nickel ions and, dissolved therein, an effective amount of a brightener of the general formula

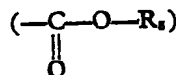


wherein:

- $R_1$  is selected from the group consisting of methyl, ethyl and hydroxyethyl;  
 $R_2$  is selected from the group consisting of alkenyl, alkynyl, hydroxy-substituted alkynyl and lower alkyl-substituted alkynyl;  
 $R_3$  is lower alkylene, lower alkoxyalkylene, lower alkenylene, lower alkoxy-alkenylene, hydroxy-substituted lower alkylene, carboxy-substituted lower alkylene and hydroxy- and N-methyl-substituted lower aminoalkylene;  
 $R_4$  is selected from the group consisting of a sulphonic radical ( $-\text{SO}_3^-$ ), a carboxy radical



or an aliphatic carboxy-ester group



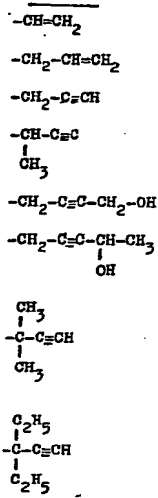
where  $R_s$  is alkyl, alkenyl, alkynyl, alkoxyalkynyl, hydroxyalkoxyalkynyloxy-alkyl, or a corresponding halogen-substituted radical, hydroxyalkyl, hydroxy-alkenyl, hydroxyalkynyl, haloalkyl, halohydroxyalkyl, halohydroxyalkynyl, hydroxyalkoxyalkynyl or alkynyloxyalkyl; and

X is selected from the group consisting of halogen and hydroxy when the positive charge on the nitrogen atom is not otherwise neutralized and X is absent when said charge is neutralized by another substituent of the molecule.

A lower radical or group should be understood to contain up to 6 carbon atoms. Some suitable Examples of  $R_2$  are listed in Table 1.

Examples of  $R_2$ 

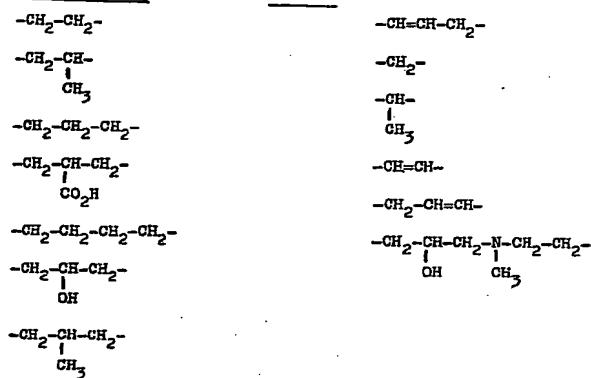
Table 1



Some suitable examples of  $R_3$  are listed in Table 2.

Examples of  $R_3$ 

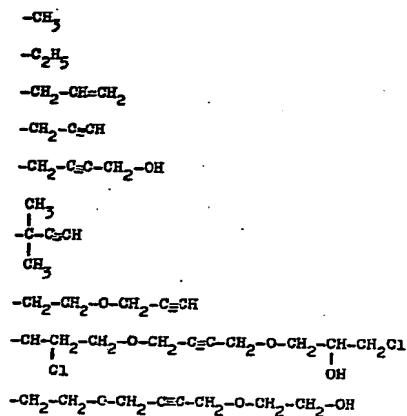
Table 2



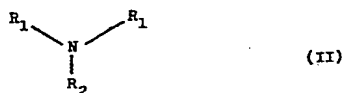
Some suitable examples of  $R_5$  are listed in Table 3.

Examples of  $R_5$ 

Table 3



The compounds of formula I may be prepared by reacting an aliphatic, unsaturated (olefinic or acetylinic) tertiary amine of the general formula



wherein  $R_1$  and  $R_2$  have the meanings given above, with a quaternizing agent which is:

- |    |   |    |
|----|---|----|
| 5  | (a) an aliphatic, alpha-beta unsaturated carboxylic acid or an aliphatic ester thereof;                     | 5  |
|    | (b) a haloalkyl sulphonic acid or a salt, preferably an alkali metal salt, thereof;                         |    |
|    | (c) a haloalkylamino sulphonic acid or a salt, preferably an alkali metal salt, thereof;                    |    |
| 10 | (d) an alkanesultone;   | 10 |
|    | (e) a haloalkene sulphonic acid or a salt, preferably an alkali metal salt thereof;                         |    |
|    | (f) an aliphatic unsaturated sulphonic acid or a salt, preferably an alkali metal salt thereof;             |    |
| 15 | (g) a saturated aliphatic, halogenated carboxylic acid or a salt, preferably an alkali metal salt, thereof; | 15 |
|    | (h) an aliphatic ester of an aliphatic, halogenated carboxylic acid.  |    |

The quaternization reaction is carried out in known manner, preferably in an aqueous or alcoholic medium and at a temperature in the range of from 50 to 110°C. The reaction may be catalysed, if desired, by acid or base, depending on the nature of the quaternising agent. Preferably equimolar proportions of the reactants are used.

Table 4 lists some examples of suitable tertiary amines of the general formula II, Table 5 lists some examples of suitable quaternising agents, and Table 6 lists some examples of compounds of the general formula I which may be used as primary brighteners in nickel electroplating baths, along with their optimal concentration when used in such a bath.

Table 4 - Unsaturated Amines  $(R_2-N \begin{array}{l} \nearrow R_1 \\ \searrow R_1 \end{array})$

1) Dimethyl-vinylamine	$(CH_3)_2N-CH=CH_2$
2) Diethyl-vinylamine	$(C_2H_5)_2N-CH=CH_2$
3) Dimethyl-allylamine	$(CH_3)_2N-CH_2-CH=CH_2$
4) Diethanol-allylamine	$(HOCH_2CH_2)_2N-CH_2-CH=CH_2$
5) 1-Dimethylamino-propyne-2	$(CH_3)_2N-CH_2-C \equiv CH$
6) 1-Diethylamino-propyne-2	$(C_2H_5)_2N-CH_2-C \equiv CH$
7) 1-Diethanolamino-propyne-2	$(HOCH_2CH_2)_2N-CH_2-C \equiv CH$
8) 3-Dimethylamino-butyne-1	$(CH_3)_2N-CH(CH_3)-C \equiv CH$
9) 4-Diethylamino-2-butyne-1-ol	$(C_2H_5)_2N-CH_2-C \equiv C-CH_2OH$
10) 1-Diethylaminopentyne-2-ol-4	$(C_2H_5)_2N-CH_2-C \equiv C-CH(OH)-CH_3$

Table 5 -Quaternising Agents

(a)	
1) Acrylic acid	$\text{CH}_2 = \text{CH} - \text{COOH}$
2) Methacrylic acid	$\text{CH}_2 = \text{C}(\text{CH}_3) - \text{COOH}$
3) Vinylacetic acid	$\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{COOH}$
4) Itaconic acid	$\text{CH}_2 = \text{C}(\text{COOH}) - \text{CH}_2 - \text{COOH}$
5) Methyl acrylate	$\text{CH}_2 = \text{CH} - \text{CO} . \text{O} - \text{CH}_3$
6) Allyl acrylate	$\text{CH}_2 = \text{CH} - \text{CO} . \text{O} - \text{CH}_2 - \text{CH} = \text{CH}_2$
7) Acrylate of 2-butyne-1,4-diol	$\text{CH}_2 = \text{CH} - \text{CO} . \text{O} - \text{CH}_2 - \text{C} \equiv \text{C} - \text{CH}_2 - \text{OH}$
8) Allylacetate of 2-propyne-1-ol	$\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CO} . \text{O} - \text{CH}_2 - \text{C} \equiv \text{CH}$
9) Itaconate of 2-hydroxyethoxy- -2-propyne	$\text{CH}_2 = \text{C}(\text{COOH}) - \text{CH}_2 - \text{CO} . \text{O} - \text{CH}_2 - \text{CH}_2 - \text{O} - \text{CH}_2 - \text{C} \equiv \text{CH}$
10) Acrylate of 1,4-di-(beta- hydroxyethoxy)-2-butyne	$\text{CH}_2 = \text{CH} - \text{CO} . \text{O} (\text{CH}_2)_2 \text{OCH}_2 \text{C} \equiv \text{CCH}_2 \text{O} (\text{CH}_2)_2 \text{OH}$
(b)	
11) 2-Chloroethane sulphonic acid (Na)	$\text{Cl} - \text{CH}_2 - \text{CH}_2 - \text{SO}_3 \text{Na}$
12) 3-Bromopropane sulphonic acid (Na)	$\text{Br} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{SO}_3 \text{Na}$
13) 3-Chloro-2-hydroxypropane sulphonic acid (Na)	$\text{Cl} - \text{CH}_2 - \text{CH}(\text{OH}) - \text{CH}_2 - \text{SO}_3 \text{Na}$
14) 3-Bromo-2-methylpropane sulphonic acid	$\text{Br} - \text{CH}_2 - \text{CH}(\text{CH}_3) - \text{CH}_2 - \text{SO}_3 \text{H}$
(c)	
15) N-chlorohydroxypropyl-N-methyl- Taurine (Na salt)	$\text{ClCH}_2 \text{CH}(\text{OH}) \text{CH}_2 \text{N}(\text{CH}_3) \text{CH}_2 \text{CH}_2 \text{SO}_3 \text{Na}$
(d)	
16) Propansultone	$\text{O} - (\text{CH}_2)_3 - \text{SO}_2$
17) Butansultone	$\text{O} - (\text{CH}_2)_4 - \text{SO}_2$
(e)	
18) 1-Chloro-2-propene sulphonic acid	$\text{Cl} - \text{CH}_2 - \text{CH} = \text{CH} - \text{SO}_3 \text{H}$

Table 5 (continued)

(f)

- 19) Sodium allyl sulphonate  $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{SO}_3\text{Na}$   
 20) Sodium propyne sulphonate  $\text{CH} = \text{C} - \text{CH}_2 - \text{SO}_3\text{Na}$

(g)

- 21) Sodium chloro-acetate  $\text{Cl}-\text{CH}_2-\text{CO.O Na}$   
 22) 2-Chloro-propionic acid  $\text{CH}_3-\text{CH}(\text{Cl})-\text{COOH}$   
 23) Sodium 3-chloro-propionate  $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{COONa}$

(h)

- 24) Ethyl chloroacetate  $\text{Cl}-\text{CH}_2-\text{CO.O}-\text{CH}_2-\text{CH}_3$   
 25) Allyl 3-chloro-propionate  $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{CO.O}-\text{CH}_2-\text{CH} = \text{CH}_2$   
 26) Chloro-acetate of 2-methyl-3-butyne-2-ol  $\text{Cl}-\text{CH}_2-\text{CO.O}-\text{C}(\text{CH}_3)_2-\text{C} \equiv \text{CH}$   
 27) 3-Chloro-propionate of 1,4di-(beta-hydroxy-gamma-chloro propoxy)-2-butyne  $\text{ClCH}_2\text{CH}_2\text{CO.OCH}(\text{CH}_2\text{Cl})\text{CH}_2\text{OCH}_2\text{C}\equiv\text{CCH}_2\text{OCH}_2\text{Cl}-\text{H}_2\text{C}-\text{CH}-\text{OH}$   
 28) Alpha-chloro-acrylate of 3-butyne-1-ol  $\text{Cl}-\text{CH} = \text{CH}-\text{CO.O}-\text{CH}_2-\text{CH}_2-\text{C} \equiv \text{CH}$

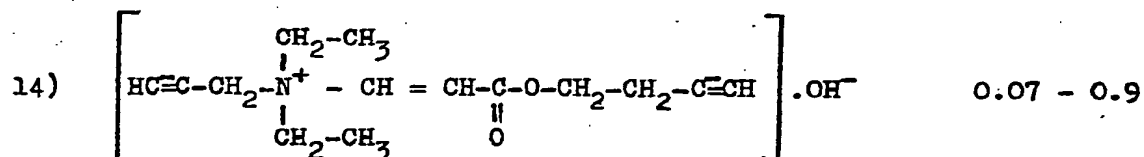
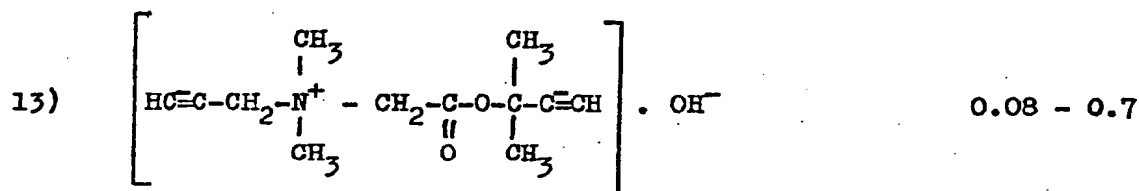
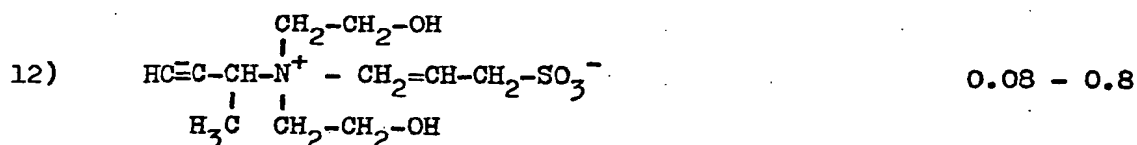
Table 6 - Brighteners of Formula (I)

<u>Compound of formula (I)</u>		<u>Optimal concentration in the nickel bath (g/l)</u>
1)	$\text{H}_2\text{C} = \text{CH} - \overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{N}^+}} - \text{CH}_2 - \text{CH}_2 - \overset{\text{O}}{\underset{\text{O}}{\text{C}}} - \text{O}^-$	0.05 - 0.5
2)	$\text{HC}\equiv\text{C}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{N}^+}} - \text{CH}_2-\underset{\text{CH}_3}{\overset{\text{O}}{\text{CH}}}-\text{C}-\text{O}^-$	0.05 - 0.6
3)	$\left[ \text{HC}\equiv\text{C}-\underset{\text{H}_3\text{C}}{\overset{\text{CH}_3}{\text{CH}}}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{N}^+}} - \text{CH}_2-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-\text{CH}_2-\text{CH}_3 \right] \cdot \text{OH}^-$	0.03 - 0.4

Table 6 (continued)

4)	$\left[ \text{HC}\equiv\text{C}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{N}^+}}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_2-\text{OH} \right] \cdot \text{OH}^-$	0.05 - 1.0
5)	$\left[ \text{H}_2\text{C}=\text{CH}-\text{CH}_2-\overset{\text{CH}_2-\text{CH}_3}{\underset{\text{CH}_2-\text{CH}_3}{\text{N}^+}}-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-\text{CH}_2-\text{C}\equiv\text{CH} \right] \cdot \text{Cl}^-$	0.05 - 0.4
6)	$\left[ \text{HC}\equiv\text{C}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{N}^+}}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{C}\equiv\text{CH} \right] \cdot \text{OH}^-$	0.03 - 0.3
7)	$\text{HC}\equiv\text{C}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{N}^+}}-\text{CH}_2-\text{CH}_2-\text{SO}_3^-$	0.05 - 1.0
8)	$\text{HC}\equiv\text{C}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{N}^+}}-\text{CH}_2-\overset{\text{OH}}{\underset{\text{OH}}{\text{CH}}}-\text{CH}_2-\text{SO}_3^-$	0.03 - 1.5
9)	$\text{CH}_3-\text{CH}-\text{C}\equiv\text{C}-\text{CH}_2-\overset{\text{CH}_2-\text{CH}_3}{\underset{\text{CH}_2-\text{CH}_3}{\text{N}^+}}-\text{CH}_2-\overset{\text{OH}}{\underset{\text{OH}}{\text{CH}}}-\text{CH}_2-\text{SO}_3^-$	0.05 - 1.5
10)	$\text{HC}\equiv\text{C}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{N}^+}}-\text{CH}_2-\overset{\text{OH}}{\underset{\text{OH}}{\text{CH}}}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{N}}}-\text{CH}_2-\text{CH}_2-\text{SO}_3^-$	0.5 - 1.3
11)	$\text{HO}-\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{N}^+}}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SO}_3^-$	0.05 - 1.2

Table 6 (continued)



The electroplating bath of the invention produces a ductile, smooth and very bright deposit of nickel, over a wide range of current densities. The primary brightening agent of the general formula I is preferably present in the bath in a concentration of from 0.01 to 3.0 g/l of bath, more preferably from 0.05 to 1.5 g/l.

The electroplating bath of the present invention may also contain secondary brighteners or "brightener carriers" as known in the art. These are aliphatic or aromatic sulphonated compounds, for example o-benzoylsulphimide, aryl sulphonates, aryl sulphonamides and unsaturated aliphatic sulphonic acids. Preferably the total concentration of the one or more secondary brighteners present is in the range of from 1.0 to 10.0 g/l. Table 7 lists some examples of secondary brighteners which may be used in a bath of the present invention. Other sulphonated compounds, in the form of free acids, alkali metal or nickel salts, may be used as secondary brighteners, for example, those described in French Patent No. 1,096,351, Table 3.

TABLE 7 - Secondary Brighteners

1)	o-Benzoylsulphimide	$\text{C}_6\text{H}_4\text{CONHSO}_2$
2)	p-Toluenesulphonamide	$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2$
3)	Sodium meta-benzene disulphonate	$\text{C}_6\text{H}_4(\text{SO}_3\text{Na})_2$
4)	Sodium benzaldehyde-o-sulphonate	$\text{C}_6\text{H}_4(\text{CHO})\text{SO}_3\text{Na}$
5)	Sodium naphthalene trisulphonate	$\text{C}_{10}\text{H}_5(\text{SO}_3\text{Na})_3$
6)	Benzene sulphonamide	$\text{C}_6\text{H}_5\text{-SO}_2\text{-NH}_2$
7)	Benzene di-sulphonimide	$\text{C}_6\text{H}_4(\text{SO}_2)_2\text{NH}$
8)	Sodium vinyl sulphonate	$\text{CH}_2 = \text{CH-SO}_3\text{Na}$

TABLE 7 (continued)

- 9) Sodium allyl sulphonate  $\text{CH}_2 = \text{CH}-\text{CH}_2-\text{SO}_3\text{Na}$
- 10) Sodium propyne sulphonate  $\text{HC} \equiv \text{C}-\text{CH}_2-\text{SO}_3\text{Na}$
- 11) Sodium propynoxy ethane sulphonate  $\text{HC} \equiv \text{C}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{SO}_3\text{Na}$

The bath of the present invention may also comprise, in addition to the compound of the general formula I, one or more other primary brightening agents known in the art for nickel electroplating, in order to further increase the brighteners and the smoothness or to affect other properties of the nickel electrodeposit. An additional primary brightener may be, for example, an acetylenic alcohol or a derivative thereof, an acetylenic amine, or an alkynoxy sulphonic acid: for example 2-butyne-1,4-diol, propargylic alcohol, methylbutynol or their derivatives obtained by reaction with ethylene oxide, propylene oxide or epichlorohydrin. The concentration of additional primary brighteners is preferably from 0.05 to 1.0 g/l and preferably the total concentration of primary brighteners in the bath, including those of the general formula I, is from 0.06 to 1.05 g/l.

The source of nickel ions in the bath is generally an aqueous solution of one or more nickel salts, for example the sulphate, chloride, sulphamate or fluoroborate. A buffering agent, for example boric acid, is preferably also present, as is an alkali metal chloride. The pH of the solution is preferably from 3.5 to 5.5. The bath may also contain a wetting agent, in order to prevent pitting of the nickel deposit.

The following Examples illustrate the invention.

#### Example 1.

Preparation of the compound No. 4 of Table 6:

140 grams (1 mole) of the mono-acrylate of 2-butyne-1,4-diol, 778.5 grams of water and 111.5 grams (1 mole) of 1-dimethylamino-propyne-2 hydrochloride are heated, with stirring, under reflux (100—105°C) for 4 hours, the pH of the reaction mixture being maintained between 3.5 and 6.5.

The solution obtained, which contains about 25% of the quaternary compound No. 4 of Table 6, may be used as a nickel electroplating brightener according to this invention.

#### Example 2.

Preparation of the compound No. 8 of Table 6:

196.5 grams (1 mole) of the sodium salt of 3-chloro-2-hydroxy-propane sulphonic acid, 1006 grams of water, 20 grams of sodium hydroxide and 119.5 grams (1 mole) of 1-dimethylamino-propyne-2 hydrochloride are heated, with stirring, under reflux (100—105°C) for 4 hours. The solution obtained, which contains about 25% of the compound No. 8 of Table 6, may be used as a nickel electroplating brightener.

#### Example 3.

A standard nickel bath of the following composition is made up:

Nickel sulphate	320 g/l
Nickel chloride	50 g/l
Boric acid	45 g/l
pH	4.0—5.0

To this basic nickel electroplating bath there are added brighteners and additives according to the following Examples.

#### Example 4.

To the bath of Example 3, there is added:

o-Benzoyl-sulphimide (Na salt)	3.0 g/l
Sodium naphthalene trisulphonate	2.0 g/l
Compound No. 4 of Table 6	0.25 g/l
Sodium lauryl sulphate	0.2 g/l



Very bright, uniform, ductile and levelled nickel deposits are obtained from this bath operating at 50—65°C temperature, 1 to 5 A/dm<sup>2</sup> cathodic current density and under cathodic agitation.

Example 5.

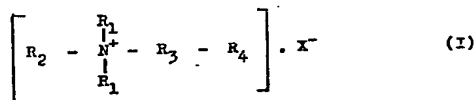
To the bath of Example 3, there is added:

o-Benzoyl sulphimide (Na salt)	2.0 g/l
Sodium propyne sulphonate	0.2 g/l
Compound No. 8 of Table 6	0.2 g/l
Compound No. 9 of Table 6	0.1 g/l
2-Butyne-1,4-diol	0.1 g/l
Sodium lauryl ether sulphate	0.1 g/l

Similar results in Example 4 are obtained.

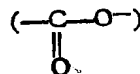
WHAT I CLAIM IS:—

1. An aqueous, acidic nickel electroplating bath which comprises a source of nickel ions and, dissolved therein, an effective amount of a brightener of the general formula

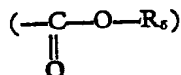


wherein:

- R<sub>1</sub> is selected from the group consisting of methyl, ethyl and hydroxyethyl;
- R<sub>2</sub> is selected from the group consisting of alkenyl, alkynyl, hydroxy-substituted alkynyl and lower alkyl-substituted alkynyl;
- R<sub>3</sub> is lower alkylene, lower alkoxyalkylene, lower alkenylene, lower alkoxy-alkenylene, hydroxy-substituted lower alkylene, carboxy-substituted lower alkylene and hydroxy- and N-methyl-substituted lower aminoalkylene;
- R<sub>4</sub> is selected from the group consisting of a sulphonic radical (—SO<sub>3</sub><sup>—</sup>), a carboxy radical



or an aliphatic carboxy-ester group



where R<sub>5</sub> is alkyl, alkenyl, alkynyl, alkoxyalkynyl, hydroxyalkoxyalkynyloxy-alkyl or a corresponding halogen-substituted radical, hydroxyalkyl, hydroxy-alkenyl, hydroxyalkynyl, haloalkyl, halohydroxyalkyl, halohydroxyalkynyl, hydroxyalkoxyalkynyl or alkynyloxyalkyl; and

X is selected from the group consisting of halogen and hydroxy when the positive charge on the nitrogen atom is not otherwise neutralized and X is absent when said charge is neutralized by another substituent of the molecule.

2. A bath as claimed in claim 1, wherein R<sub>2</sub> represents one of the groups listed in Table 1 herein.

3. A bath as claimed in claim 1, wherein R<sub>3</sub> represents one of the groups listed in Table 2 herein.

4. A bath as claimed in claim 1, wherein R<sub>4</sub> represents one of the groups listed in Table 3 herein.

5. A bath as claimed in claim 1, which comprises at least one of the compounds of the general Formula I listed in Table 6 herein.

6. A bath as claimed in any one of claims 1 to 5, wherein the total concentration of the one or more compounds of the general formula I is in the range of from 0.01 to 3.0 g/l of bath.

7. A bath as claimed in claim 6, wherein the said concentration is in the range of from 0.05 to 1.5 g/l of bath.
8. A bath as claimed in any one of claims 1 to 7, which also comprises at least one secondary brightener.
- 5 9. A bath as claimed in claim 8, wherein the secondary brightener is o-benzoyl-sulphimide, an arylsulphonate, an arylsulphonamide or an unsaturated aliphatic sulphonic acid. 5
- 10 10. A bath as claimed in claim 9, wherein the secondary brightener is one of the compounds listed in Table 7 herein. 10
11. A bath as claimed in any one of claims 8 to 10, wherein the total concentration of the one or more secondary brighteners is in the range of from 1.0 to 10.0 g/l of bath.
12. A bath as claimed in any one of claims 1 to 11, which also comprises at least one other primary brightener known in the art.
- 15 13. A bath as claimed in claim 12, wherein the other primary brightener is an acetylenic alcohol or a derivative thereof, an acetylenic amine, or an alkynoxy sulphonic acid. 15
14. A bath as claimed in claim 13, wherein the other primary brightener is 2-butyne-1,4-diol, propargylic alcohol, methylbutynol, or the reaction product of one of these alcohols with ethylene oxide, propylene oxide or epichlorohydrin.
- 20 15. A bath as claimed in any one of claims 12 to 14, wherein the total concentration of the other primary brighteners is in the range of from 0.05 to 1.0 g/l of bath. 20
16. A bath as claimed in any one of claims 1 to 15, wherein the source of nickel ions is nickel sulphate, nickel chloride, nickel sulphamate or nickel fluoroborate, or a mixture of two or more of these salts.
- 25 17. A bath as claimed in claim 1, substantially as described in either Example 4 or Example 5 herein. 25
18. A method of electroplating an article with nickel, which comprises using a bath as claimed in any one of claims 1 to 17, wherein the article to be electroplated forms the cathode.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1979.  
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.